JOURNAL OF SOLID STATE CHEMISTRY 52, 197–202 (1984)

Crystal Structure and Properties of the Uranium Chalcogenides α-US_2 and α-USe_2

H. NOEL AND J. Y. LE MAROUILLE

Université de Rennes-Beaulieu, Laboratoire Associé au CNRS N°254, Laboratoire de Chimie du Solide et Inorganique Moléculaire, Avenue du Général Leclerc, 35042 Rennes Cédex, France

Received May 17, 1983; in revised form October 24, 1983

The uranium chalcogenides α-US_2 and α-USe_2 crystallize in the tetragonal space group *P4/ncc* and not *I4/mcm* as previously reported. Their crystal structures have been determined from single-crystal X-ray diffraction data and refined to $R = 0.041$ and $R = 0.034$, respectively. Uranium atoms occupy two crystallographic sites: U(1) in (8*f*) and U(2) in (4*c*). The fourfold position, U(2), is incompletely filled with three uranium atoms which show a significant uniaxial delocalization. Properties are discussed in relation to this new crystal structure.

Introduction

Most of crystal structures of the uranium chalcogenides known so far are from the pioneering work of Zachariasen (*1*), from X-ray powder diffraction (*2, 3*), or simply by assuming isomorphism with other binaries. In order to go deeper in the study or interpretation of the physical properties of these compounds, their structural parameters have to be refined using single-crystal diffraction data. We have shown that valuable informations concerning the electronic state of uranium may be obtained from uranium–chalcogen distances analysis (*4*). Furthermore, some structural framework particularities have to be reexamined: a structure model of tetragonal α-US_2 was reported twenty years ago (*2*) and in spite of some uncertainties about space group and sulfur positions, it could be settled that the nonstoichiometry of α-US_2 and α-USe_2 must be understood in terms of vacancies in one of the uranium positions (*5*). Incomplete and variable atomic filling of a crystallographic site is a very promising property in materials, since it is one of the important factors in favoring atomic mobility in the solid state.

Experimental

Single crystals of the tetragonal phases α-US_2 and α-USe_2 were grown by the gas-phase transport method, using bromine (UBr_4) as transporting agent and a temperature gradient of 930–840°C (*6*). Preliminary studies of these crystals by Weissenberg and Laüe methods revealed that the space group (*I4/mcm*) so far assumed (*2*) for this structural type, is incorrect. The systematic extinctions: $hk0: h + k = 2n + 1$, $0kl: l = 2n + 1$, $hhl: l = 2n + 1$, are consistent with the space group *P4/ncc* (D_{4h}^8). It follows that the previously reported (*2*) crystal structure of α-US_2 is erroneous.

0022-4596/84 $3.00

TABLE I

LATTICE CONSTANTS AND SOME CRYSTAL STRUCTURE DETERMINATION PARAMETERS

	α-US_2	α-USe_2
Space group	$P4/ncc$	$P4/ncc$
Lattice constants	$a = b = 10.293(1)$ $c = 6.374(4)$	$a = b = 10.765(1)$ $c = 6.660(4)$
Wavelength λ Mo$K\alpha$	0.71073 Å	0.71073 Å
Scan range 2θ	2–60°	2–60°
μr	4.3	4.5
Number of independent measured reflections ($\dot{I}$)	495	569
Number of observed reflections ($\dot{I} > 2\sigma(\dot{I})$)	302	346
$R = \Sigma\lvert\lvert F_0\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_0\rvert$	0.041	0.034
$R_\omega = \left\lvert\frac{\Sigma\omega(\lvert F_0\rvert - \lvert F_c\rvert)^2}{\Sigma\omega\lvert F_0\rvert^2}\right\rvert^{1/2}$	0.058	0.041
Number of varied parameters	23	23
Goodness of fit $(\Sigma\omega(F_0 - F_c)^2/m - n)^{1/2}$	1.567	1.048
Weighting scheme (based on counting statistics)	$\frac{1}{\omega} = \sigma_F^2 = \frac{1}{4}\left\lvert\frac{\sigma_{\dot{I}}^2}{\dot{I}} + (0.06\,\dot{I})\right\rvert^2$	

X-Ray diffraction intensities (Mo$K\alpha$ radiation) have been collected using an automatic four circle diffractometer, from α-US_2 and α-USe_2 single crystals selected with isotropic dimensions allowing spherical-type absorption corrections. The lattice constants of the crystals investigated and important X-ray data collection parameters are given in Table I.

Crystal Structure Determination

All calculations were performed on a PDP 11/60 computer using the SDP package (7). The positions of the uranium atoms have been determined by the deconvolution of the Patterson function, and the positional parameters of the chalcogen atoms were obtained from a Fourier difference synthesis. Uranium was found to occupy two crystallographic sites U(1) in (8*f*) and U(2) in (4*c*), and the chalcogens to be located in (16*g*) and (4*b*) positions. This leads to a crystallographic formula $U_{12}X_{20}$ (X = S, Se). An unreliable value of the U(2) isotropic thermal parameter suggested that the mean electron density in the (4*c*) crystallographic site is lower than that corresponding to full occupancy by uranium. Subsequent least-square refinements led to similar values 0.752 and 0.744 of the U(2) occupancy factors in α-US_2 and α-USe_2, respectively. This means that, in both crystals, approximately three uranium atoms are randomly distributed over four U(2) positions. The crystallographic formula is then $U_{11}X_{20}$, which corresponds to the X/U ratio 1.82, in fair agreement with other pre-

TABLE II

FRACTIONNAL ATOMIC COORDINATES OF α-US_2, WITH ESD'S IN PARENTHESES. τ IS THE OCCUPANCY FACTOR

Atom	τ	X	Y	Z
U1	1	0.59603(6)	0.40397(6)	0.250
U2	0.752(5)	0.250	0.250	0.8642(7)
S1	1	0.0406(5)	0.3387(4)	0.119(1)
S2	1	0.750	0.250	0.000

TABLE III

FRACTIONAL ATOMIC COORDINATES OF α-USe$_2$, WITH ESD'S IN PARENTHESES. τ IS THE OCCUPANCY FACTOR

Atom	τ	X	Y	Z
U1	1	0.59536(5)	0.40464(5)	0.250
U2	0.744(4)	0.250	0.250	0.8635(5)
SE1	1	0.0405(2)	0.3379(1)	0.1194(3)
SE2	1	0.250	0.750	0.500

vious studies (5). After several refinement cycles of the positional parameters, occupancy factors and anisotropic thermal parameters, the residual factor converged to the final values $R = 0.041$ and $R = 0.034$ for α-US$_2$ and α-USe$_2$, respectively.

Tables II to V give the refined positional and thermal parameters of these two isomorphous compounds.

Crystal Structure Description

Figure 1 displays a projection of the crystal structure of α-US$_2$ in the (a, b) plane. Uranium U(1) is bonded to eight sulfur atoms: six S(1) and two S(2) forming a distorted antiprismatic type coordination polyhedron (Fig. 2). Uranium U(2) is coordinated by eight S(1) atoms forming a regular square antiprism (Fig. 3), the square faces of which are represented with dotted lines on Fig. 1. The uranium–chalcogen and the shortest chalcogen–chalcogen distances are reported in Table VI.

Discussion

This crystal structure raises very interesting features in the physics and solid state chemistry of uranium.

1. Crystal Structure and Electronic Structure of Uranium

The electronic configuration of uranium, i.e., the uranium ion $5f$ electron number, cannot in general be assigned conclusively from the usual physical constants such as the paramagnetic moment. In α-US$_2$ and α-USe$_2$, the electroneutrality principle applied to the chemical formula $U_{1.1}X_2$ leads to a formal uranium valence equal to 3.6, representing the number of uranium electrons involved in bonding. The electrical conductivities of these binaries are not yet really known but the conduction band electron population can probably not be neglected in such compounds, and thus should be taken into account in deriving the effective uranium valence.

As the uranium ion size is sensitive to the $5f$ electron number, we have shown (*4*) that the latter may be estimated from correlations with the average U–X distances, obtained from crystal data. In α-US$_2$ and α-USe$_2$, the average bond lengths: U(1)–S = 2.85 Å, U(2)–S = 2.83 Å, U(1)–Se = 2.98

TABLE IV

ANISOTROPIC ($B(i,j)$) AND EQUIVALENT ISOTROPIC (BEQV (Å^2)) THERMAL PARAMETERS OF α-US$_2$

Atom	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$	BEQV (Å^2)
U1	0.83(2)	$B(1,1)$	1.42(3)	0.12(2)	0.05(4)	$B(1,3)$	1.03(1)
U2	0.83(3)	$B(1,1)$	5.4(1)	0	0	0	2.37(4)
S1	1.1(1)	0.7(1)	1.7(2)	−0.2(1)	0.1(2)	−0.0(2)	1.19(7)
S2	1.0(2)	$B(1,1)$	1.4(3)	0	0	0	1.13(9)

Note. The form of the anisotropic thermal parameter is $\exp(-1/4\ \Sigma_{ij} h_i h_j a_i^* a_j^* B(i,j))$, where a^* is a reciprocal lattice constant.

TABLE V

ANISOTROPIC ($B(i,j)$) AND EQUIVALENT ISOTROPIC (BEQV (Å^2)) THERMAL PARAMETERS OF α-USe$_2$

Atom	$B(1,1)$	$B(2,2)$	$B(3,3)$	$B(1,2)$	$B(1,3)$	$B(2,3)$	BEQV (Å^2)
U1	1.03(1)	$B(1,1)$	1.64(2)	0.13(2)	0.09(3)	$B(1,3)$	1.233(8)
U2	0.93(3)	$B(1,1)$	5.2(1)	0	0	0	2.35(3)
SE1	1.22(5)	1.04(5)	1.83(5)	−0.04(4)	−0.14(6)	−0.03(5)	1.37(2)
SE2	1.09(5)	$B(1,1)$	1.53(9)	0	0	0	1.23(3)

Note. The form of the anisotropic thermal parameter is $\exp(-1/4\ \Sigma_{ij} h_i h_j a_i^* a_j^* B(i,j))$, where a^* is a reciprocal lattice constant.

Å, U(2)–Se = 2.96 Å are close to the values 2.82 ± 0.02 and 2.97 ± 0.02 Å (for X = S and Se) found to be characteristic of the mean U–X distances for uranium in the tetravalent state and eightfold coordination. Although the above range of reference distances ±0.02 Å (due mainly from polyhedron distortion) may imply a limit to further interpretation, the different shifts of U–S and U–Se distances relative to the reference values suggest that both U(1) and U(2) have higher crystal radii in the sulfide than in the selenide, hence that U(1) may have some intermediate valence character in α-US$_2$. In other words, these data suggest a slightly higher electron delocalization, or conduction band population, in the selenide than in the sulfide.

TABLE VI

INTERATOMIC DISTANCES (Å), WITH ESD'S IN PARENTHESES

	X = S	X = Se
U(1)–X(2)	2.750(0) × 2	2.883(0) × 2
U(1)–X(1)	2.820(5) × 2	2.951(2) × 2
U(1)–X(1)	2.836(4) × 2	2.965(1) × 2
U(1)–X(1)	2.986(4) × 2	3.116(2) × 2
U(2)–X(1)	2.815(5) × 4	2.937(2) × 4
U(2)–X(1)	2.847(5) × 4	2.981(3) × 4
U(2)–U(2)	3.187(0)	3.330(0)
U(1)–U(2)	3.966(1)	4.143(1)
U(1)–U(1)	4.239(0)	4.418(0)
X(2)–X(2)	3.187(0)	3.330(0)
X(1)–X(2)	3.218(4)	3.362(2)
X(1)–X(1)	3.310(0)	3.459(2)
X(1)–X(1)	3.384(0)	3.542(3)

2. *Crystal Structure and Magnetic Properties*

Although α-US$_2$ and α-USe$_2$ are isomorphous, they have been reported to behave somewhat differently at low temperature. A transitional λ-type anomaly was reported to occur in α-USe$_2$ at T = 13.1 K while only Schottky-type anomalies were observed in the sulfide (*8*). Powder magnetization measurements (*9*) confirmed the setting up of magnetic order in α-USe$_2$ and are not conclusive on α-US$_2$. Accounting of the very low entropy of the α-USe$_2$ magnetic transition, it was postulated (*8*) that only a small fraction of uranium, corresponding to the U(2) atoms in this refined structure, was involved in cooperative ordering. The distances between the U(2) crystallographic sites are equal to $c/2$ and so are very short: 3.19 and 3.33 Å in α-US$_2$ and α-USe$_2$, respectively. As these positions are occupied with 3/4 probability, these are effective distances between two consecutive U(2) ions.

Some years ago, Hill defined a U–U spacing limit, approximately 3.4 Å, below which no magnetic ordering is expected to occur (*10*), the shortening of interatomic distances, and the correlated f–f overlap and electron delocalization, favoring the appearance of Pauli paramagnetism and

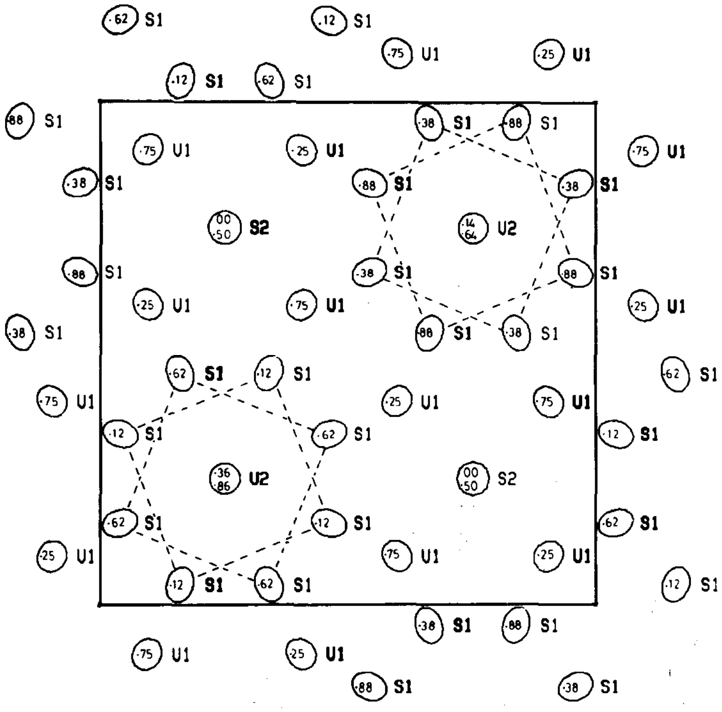

FIG. 1. Projection of the crystal structure of α-USe in the (a, b) plane with the z coordinate of each atom.

even superconductivity in some intermetallics. The U(2)–U(2) spacing is far below the Hill limit in the sulfide, but close to it in the selenide, which could account for differences in some low temperature properties. However, the nonintegral occupancy, implying breaks in the U(2)–U(2) chains, is not favorable to spin ordering in this sublattice, neither in the sulfide or in the selenide. The correct crystal structure being known, this question will now be resolved via neutron diffraction experiments.

3. Crystal Structure and Uranium Mobility

From Figs. 1 and 3, one can observe several features. Antiprisms of S(1) atoms, sharing the square faces, form a pseudochannel running along the [001] direction.

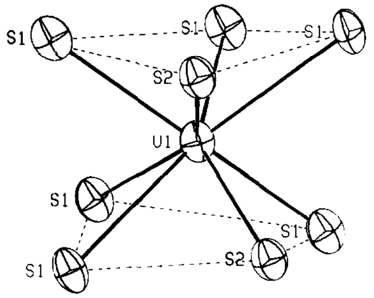

FIG. 2. Environment of U(1).

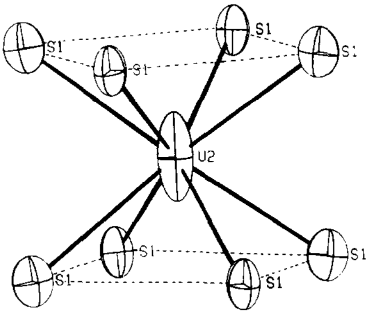

FIG. 3. Environment of U(2). Thermal ellipsoids are drawn at 90% probability.

According to the very high value of the B_{33} anisotropic thermal parameters of U(2) (Tables IV and V), both in α-US_2 and α-USe_2, the thermal ellipsoids (Fig. 3) are much elongated in the *c* axis direction (excentricity 7). These ellipsoids give a picture of the uranium position, averaged over time and space, and are indicative of some U(2) delocalization along the pseudo channel axis.

Furthermore, both α-US_2 and α-USe_2 are known to accomodate a rather wide range of nonstoichiometry with subsequent lattice parameter variations (*3, 5*). Although the reported formulas (*3, 5*) reflect more the starting S/U and Se/U ratios before reactions than the effective phase composition, we can assume that the non-stoichiometry extends close to the limiting ratio values $X/U = 1.67$ (U_3X_5) and $X/U = 2$ (UX_2). These limits correspond respectively to the filling (4/4) and half (2/4) filling of the (4*c*) U(2) crystallographic site. The crystal framework remaining unchanged upon the filling process, this behaviour may be considered as an inward motion of uranium, which can occur at high temperatures.

The diagonal $X(1)$–$X(1)$ spacings in the antiprism square faces are respectively equal to 4.68 and 4.89 Å for X = S and Se. They determine the size of the potential conduction path and are probably not large enough to allow the corresponding outward motion of U(2) at ambient temperature. If such a mobility could be achieved, it would open the possibility of partially separating the U(2) from the lattice.

References

1. W. H. Zachariasen, *Acta Crystallogr.* **2,** 291 (1949).
2. R. C. L. Mooney-Slater, *Z. Kristallogr.* **120,** 278 (1964).
3. E. W. Breeze and N. H. Brett, *J. Nucl. Mat.* **40,** 113 (1971).
4. H. Noel, *J. Solid State Chem.* **52,** 203 (1984).
5. F. Gronvold, H. Haraldsen, T. Thurmann-Moe, and T. Tufte, *J. Inorg. Nucl. Chem.* **30,** 2117 (1968).
6. V. K. Slovyanskikh, V. G. Sevast'Yanov, and G. V. Ellert, *Russ. J. Inorg. Chem.* **15**(8), 1064 (1970).
7. B. A. Frenz, The Enraf-Nonius CAD-4 SDP. A Real Time System for Concurrent X-Ray Collection and Crystal Structure Determination. "Computing in Crystallography" (H. Schenk, R. Olthof-Hazekamp, H. Van Koningsveld, and G. C. Bassi, Eds.), p. 64, Delft Univ. Press (1978).
8. E. F. Westrum and F. Gronvold, *J. Inorg. Nucl. Chem.* **32,** 2169 (1970).
9. W. Suski, A. Czopnik, and T. Mydlarz, *Phys. Status Solidi A* **12,** 525 (1972).
10. H. H. Hill, "Plutonium 1970 and Other Actinides" (W. N. Miner, Ed.), p. 2, The Metallurgical Society of the AIME, New York (1970).